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Phenanthrene and Methylphenanthrene Isomers in Maturity Assessment of Biodegraded Crude Oils (Sakhalin, Russia)

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Abstract

This paper is aimed at defining two new advantageous maturation parameters based on distribution and abundance of phenanthrene (P) and methylphenanthrene (MP) isomers in the tricyclic fraction of aromatic hydrocarbons: MPI 3+1/PAI 1 and [2(2-MP+3-MP)+P]/1-MP. The applicability of newly proposed parameters was checked by correlation analysis. Depth of the reservoir rock, diasterane maturation parameter, as well as several typical aromatic fraction maturation parameters were used for this purpose. The examined oils (fourteen samples from nine oil fields of Sakhalin Island, Russia), were of Miocene age and from reservoir rocks of relatively wide range of depths (73-2841 m). All samples represented biodegraded, or mixtures of biodegraded and nonbiodegraded oils [1].

Introduction

Structural changes of methylphenanthrene (MP) isomers in sediments are pretty well understood. They were found to consist mainly of the transformation of α-isomers (1-MP and 9-MP) into thermodynamically more stable β-isomers (2-MP and 3-MP), as well as dealkylation of both α- and β-isomers yielding phenanthrene (P). Hence, important maturation parameters based on crude oil tricyclic aromatic fraction constituents resulted from the investigation of these reactions [2,3]. The corresponding parameters most frequently used were the following: methylphenanthrene index 1 MPI 1 = 1,5 (2-MP+3-MP)/(1-MP+9-MP+P) [4], methylphenanthrene index 3 MPI 3 = (2-MP+3-MP)/(1-MP+9-MP) [5,2], phenanthrene parameter 1 PP 1 = 1-MP/(2-MP+3-MP) [6], phenanthrene alkylation index 1 PAI 1 = (1-MP+2-MP+3MP+9-MP)/P [7] and methylphenanthrene ratio 1 MPR 1 = 2-MP/1-MP [8].

Considering the fact that crude oil aromatic hydrocarbons in reservoir rocks are much more resistant towards microorganisms than its alkane constituents [9], MP-P maturation parameters are particularly useful and important in correlation studies of biodegraded crude oils. Thus, for example, fourteen samples of biodegraded crude oils originating from Sakhalin Island (Russia) oil fields were recently classified, according to maturation degree based on maturity parameter MPI 3, into three groups [1]. Moreover, investigating the same fourteen samples of biodegraded oils, it was shown that the content of phenanthrene in the tricyclic aromatic fraction, [P], may also be successfully used for the assessment of crude oil maturity. High maturity crude oils were suggested to contain more than 14% phenanthrene, crude oils of moderate maturity between 7 and 14%, and crude oils of low maturity less than 7% phenanthrene in the tricyclic aromatic fraction [1].

Favourable properties of the available set of crude oils originating from the Sakhalin Island oil fields, *i.e.*, in the first place the wide range of depths of their reservoir rocks (73-2841 m), but also their maturation degree heterogeneity [1], aroused our interest in widening the list of reliable maturation parameters, preferably based on both isomerization and dealkylation processes of methylphenanthrenes. The rational

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for this interest was found in the belief that a larger number of reliable maturation parameters may only be helpful in any future correlation study of biodegraded oils.

Consequently, in this paper the contents of all individual MP isomers as well as P were first correlated with the reservoir rocks depths, aimed at checking whether their usage for defining maturation parameters was justified. Since significant positive correlations were observed, two novel maturation parameters were proposed. Having in mind that isomerization of phenanthrene α-methyl isomers into β-isomers, as well as their dealkylation into phenanthrene, do represent two basic maturation processes of methylphenanthrene isomers in crude oils, parameters involving both mentioned types of transformation processes were considered to be advantageous as maturation parameters.

Experimental

Fourteen crude oil samples of Miocene age from nine Sakhalin Island (Russia) oil fields were analyzed in this paper. The list of samples, including data on the wide range of reservoir rock depths (73-2841 m), together with the wide range of formation pressures (2-25 MPa) and temperatures (9-86°C) is shown in Table 1. All samples were either biodegraded or were mixtures of biodegraded and nonbiodegraded crude oils [1].

Methylphenanthrene isomers as well as phenanthrene itself were identified by gas chromatographic analysis of the tricyclic aromatic hydrocarbons' fraction (Biochrom 3700, quartz capillary column; SE-54; He carrier gas; FID) [10,3]. Identification of individual isomers was based on comparison with a mixture of standards, and their proportions were determined by computer data processing (Shimadzu, Model ICR, 1B). Locations of the oil fields, together with geological data on the whole basin, as well as analytical methods and instrumental techniques applied, were described in detail elsewhere [1].

Results and discussion

The proportions of methylphenanthrene isomers 1-MP and 9-MP (α-isomers) and 2-MP and 3-MP (β-isomers), as well as phenanthrene itself, determined in the tricyclic aromatic fraction of fourteen samples examined, are shown in Table 2.

Significant positive correlations were observed

Table 1

List of crude oil samples, together with reservoir depths and the wide range of formation pressures and temperatures.

Sample No	Field	Reservoir depth (m)
1	Kolendo	1489
2	Okha	1190
3	Okha	586
4	Okha	73
5	Ekhabi	514
6	Eastern Ekhabi	794
7	Eastern Ekhabi	710
8	Eastern Ekhabi	219
9	Sabo	1983
10	Paromai	956
11	Paromai	929
12	Low Dagi	2841
13	Mongi	2203
14	Katangli	128

Formation pressure range 2-25 MPa
Formation temperature range 9-86°C

Table 2

Values of parameter Dr and proportions of (MP), (P) and anthracene (A) in crude oils (relative to total tricyclic aromatic hydrocarbons), %.

No	Dr	1-MP	9-MP	2-MP	3-MP	P	A
1	0.605	8.58	9.91	10.02	9.80	11.68	0.35
2	0.640	8.22	11.11	8.22	10.44	10.22	0.32
3	0.625	6.90	8.58	7.65	8.21	8.58	0.58
4	0.610	6.50	10.13	4.16	3.84	4.37	0.64
5	0.630	8.07	8.91	8.07	8.57	11.76	0.58
6	0.643	8.36	10.20	8.50	8.22	13.31	0.57
7	0.619	8.60	11.17	10.46	11.75	13.18	0.72
8	0.629	6.61	8.81	8.72	7.34	11.74	0.69
9	0.652	7.33	10.81	10.62	13.37	20.88	0.48
10	0.632	9.65	9.18	8.16	8.63	13.73	0.49
11	0.623	8.66	8.66	8.74	9.15	12.86	0.37
12	0.672	9.17	7.72	10.42	8.69	15.44	0.30
13	0.656	7.97	9.36	9.19	11.09	17.85	0.35
14	0.600	4.70	2.78	3.08	2.60	6.05	1.54

between the proportions of these relevant constituents of tricyclic aromatic fraction and the corresponding crude oil reservoir rock depths (Table 3; Fig. 1). In correlations of [P] with the reservoir rock depths, calculation of correlation coefficients was based on logarithmic dependence (Table 3; Fig. 1a), since during the process of maturation the proportion of phenanthrene first increased to a maximum, remaining constant afterwards. In this particular case the logarithmic curve reached a maximum at the depth of approximately 2500 m.

Table 3

Results of correlaton analyses: proportions of phenanthrene and methylphenanthrene isomers in tricyclic aromatic fraction – reservoir rock depths.

Parameters	r(p) [*a] Mathematical equation	Grafic on figure
Y↓ X →	Depth	↓
[P] (%)	0.819 (0.000) $y = 3.286 \ln(x) - 9.265$	1(a)
2-MP (%)	0.777 (0.001) $y = -1.24 \cdot 10^{-6}x^2 + 0.0053x + 4.94$	1(b)
3-MP (%)	0.859 (0.000) $y = -2.54 \cdot 10^{-6}x^2 + 0.009x + 3.63$	1(c)
1-MP (%)	0.690 (0.010) $y = -8.45 \cdot 10^{-7}x^2 + 0.0031x + 5.98$	1(d)
9-MP (%)	0.565 (0.050) $y = -1.63 \cdot 10^{-6}x^2 + 0.005x + 6.71$	1(e)

[*a] r – correlation coefficient; p – degree of reliability

On the other hand, in MP isomers – reservoir rock depths correlations, correlation coefficients were calculated from quadratic dependence. Compared to logarithmic or linear dependence, from the point of view of organic geochemistry, the quadratic dependence seemed to be much better grounded. Namely, in this particular case, with the maturation processes progressing, the proportion of the corresponding isomers increased in the earlier stages and gradually decreased after reaching a maximum. The parabolic curve representing the correlation of the most stable methylphenanthrene, 2-MP (Dewar number: 2.18; [2]) showed a theoretical maximum at approximately 2000 m, while that the thermodynamically least stable isomer, 9-MP (Dewar number: 1.80; [2]) had a maximum at smallest depths of *ca.* 1500 m (Table 3; Fig.1; *b* and *e*, respectively). This observation was quite logical, since the concentration of the most stable isomer, 2-MP, was beginning to decrease in the later stages of maturation processes (*i.e.*, at greater depths)

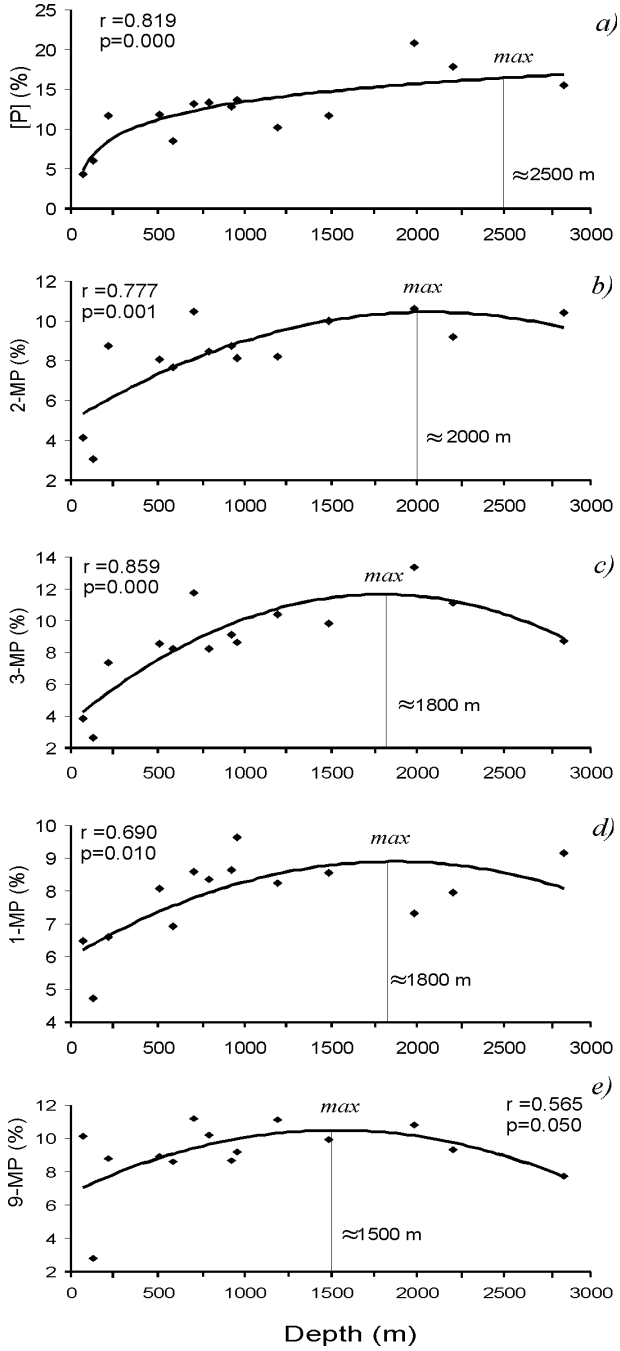

Fig. 1. Correlation diagrams: (*a*) logarithmic dependence [*P*] - *depth*; (*b* and *c)* quadratic dependence β-*isomers* – *depth*; *(d* and *e*) quadratic dependence α-*isomers* – *depth*.

compared to the least stable isomer, 9-MP. On the other hand, due to a higher stability of phenanthrene compared to MP isomers, the parabolic curves were reaching a maximum at lower depths compared to the corresponding logarithmic [P] - depths curve (*i.e.*, 1500-2000 m relative to 2500 m; Table 3; Fig. 1).

The results observed suggested that the processes of isomerization and dealkylation of methylphenanthrene isomers in the investigated set of crude oil

samples for the most part occurred during their maturation in reservoir rocks. Hence, these observations justified, once more, the usage of methylphenanthrene isomers and phenanthrene concentrations for defining crude oil maturation parameters. Consequently, benefiting from the circumstance of having a unique set of biodegraded crude oil samples, which, moreover, demonstrated significant positive correlations of methylphenanthrene isomers and phenanthrene – reservoir rock depths, in this paper two new parameters are proposed as crude oil maturation parameters which combine both methylphenanthrene isomers processes:

a) **MPI 3 + 1/PAI 1,** as maturation parameter which involves isomerization processes (MPI 3; [5,2]) and dealkylation processes (PAI 1; [7]); and
b) **[2(2-MP + 3-MP) + P]/1-MP,** as parameter aimed at avoiding the known problems involved in the application of 9-MP in crude oil maturity assessment [2,11-13]. A newly proposed parameter is based on isomerization processes (1-MP → 2- and 3-MP), but, in contrast to parameter PP 1 which was proposed earlier [6], it includes dealkylation reactions of methylphenanthrenes as well. Isomerization processes being energetically more favourable than dealkylation processes, a factor 2 was introduced ahead of the sum of β-isomers.

In order to check the reliabiliy of the MPI 3 + 1/PAI 1 maturation parameter, the values calculated for the 14 examined crude oil samples were correlated (linear dependence) with the reservoir rock depths as well as with other parameters not significantly influenced by biodegradation: diasterane ratio Dr = ΣC_{27}–C_{29} (S) diasterane/ΣC_{27}–C_{29} (R+S) diasterane [14,9], MPI 3, 1/PP 1, MPR 1, phenanthrene anthracene ratio (P/A; [10]) and content of phenanthrene in the tryciclic aromatic fraction [P] (Table 4; Fig. 2). To carry out the correlation analysis, the parameters used should have the Gaussian distribution. It was checked using the Kolmogorov-Smirnov test [15]. According to the Kolmogorov-Smirnov test, there was no statistically significant difference between the empirically obtained Dr (Z = 0.471; Asymp. Sig = 0.979), MPI 3 (Z = 0.642; Asymp. Sig = 0.804), 1/PP 1 (Z = 0.655; Asymp. Sig = 0.784), MPR 1 (Z = 0.708; Asymp. Sig = 0.699), P/A (Z = 0.378; Asymp. Sig = 0.999), [P] (Z = 0.600; Asymp. Sig = 0.864) and MPI 3+1/PAI 1 (Z = 0.868; Asymp. Sig = 0.438) and the theoretical Gaussian distribution, that is why it was possible to carry out the correlation analysis. High positive correlation coefficients were observed in all cases, *i.e.*, both when x-axis parameters were partly incorporated into the proposed MPI 3 + 1/PAI 1 parameter (Table 4; Fig. 2, *c, d, e*), as well as when this was not the case (Table 4; Fig. 2, *a, b, f, g*).

Table 4

Results of correlaton analyses: two novel parameters of crude oil maturation with reservoir rock depths as well as with other maturatoin parameters independent of biodegradation.

Correlation	r(p) [*a] Mathematical equation		Grafics on figures
	Parameters		
X↓ Y→	MPI 3 + 1/PAI 1	[2(2-MP + 3-MP) +P]/1-MP	↓
Depth	0.690 (0.006) $y = 2 \cdot 10^{-4}x + 1.13$	0.566 (0.035) $y = 0.001x + 4.78$	2(a), 3(a)
Dr	0.600 (0.023) $y = 7.68x - 3.50$	0.553 (0.040) $y = 41.02x - 20.03$	2(b), 3(b)
MPI 3	0.960 (0.000) $y = 1.25x + 0.12$	0.920 (0.000) $y = 6.89x - 0.97$	2(c), 3(c)
1/PP 1	0.807 (0.000) $y = 0.40x + 0.50$	0.979 (0.000) $y = 2.76x - 0.07$	2(d), 3(d)
MPR 1	0.817 (0.000) $y = 0.93x + 0.37$	0.940 (0.000) $y = 6.18x - 0.65$	2(e), 3(e)
P/A	0.727 (0.003) $y = 0.013x + 1.01$	0.631 (0.016) $y = 0.06x + 4.14$	2(f), 3(f)
[P] (%)	0.890 (0.000) $y = 0.054x + 0.69$	0.866 (0.000) $y = 0.30x + 2.15$	2(g), 3(g)

[*a] r – correlation coefficient; p – degree of reliability

The reliability of [2(2-MP + 3-MP) + P]/1-MP maturation parameter was checked in the same way (Table 4; Fig. 3). According to the Kolmogorov-Smirnov test, there was no statistically significant difference between the empirically obtained [2(2-MP+3-MP)+P]/1-MP (Z = 0.641; Asymp. Sig = 0.806) and the theoretical Gaussian distribution.

The correlation coefficients observed were again satisfactory, *i.e.*, they were highly positive in all cases.

Hence, based on significant positive correlations with the reservoir rock depths and diasterane ratio (Dr) as well as with the most important crude oil tricyclic aromatic hydrocarbons maturation parameters independent of biodegradation (Table 4; Figs. 2 and 3), these two new relations could have been proposed as reliable maturation parameters.

Following the above mentioned classification of the examined crude oils into high, moderate, and low maturity crude oils (MPI 3 and [P]; [1]), ranges for the new maturation parameters corresponding to these

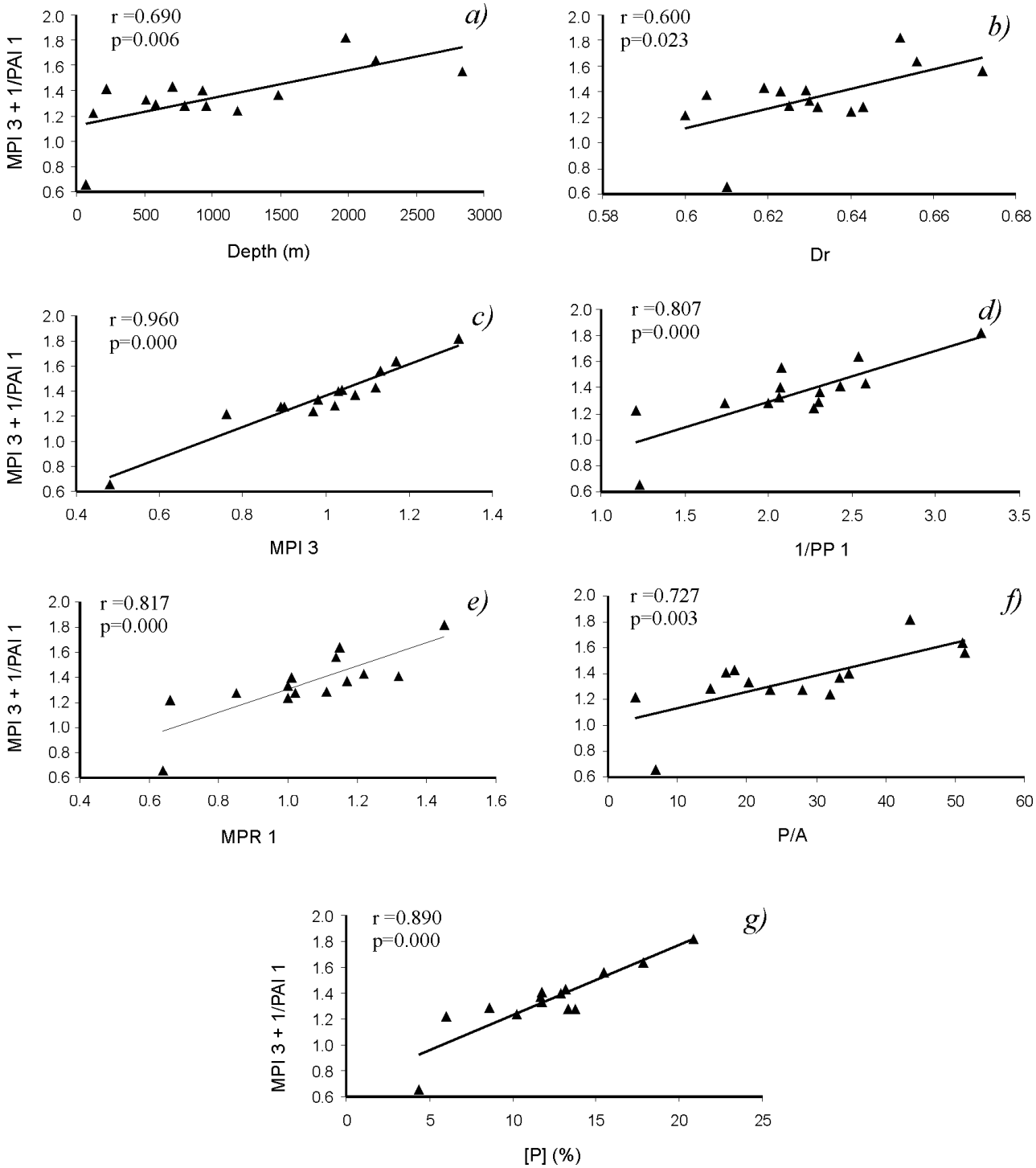

Fig. 2. Correlation diagrams: (*a*) MPI 3 + 1 PAI 1 – depth; and (*b-g*) MPI 3 + 1/PAI 1 – biodegradation independent maturation parameters.

three categories of crude oils are also suggested (Table 5; Fig. 4).

Conclusions

Two novel parameters of crude oil maturation based on tricyclic aromatic fraction constituents are proposed: MPI 3 + 1/PAI 1 and [2(2-MP + 3-MP) + P]/1-MP. Very good correlation of these parameters was observed with reservoir rock depths of fourteen variously biodegraded crude oil samples originating from the Sakhalin Island (Russia) oil fields, as well as with several maturation parameters independent of biodegradation. The following ranges of these two

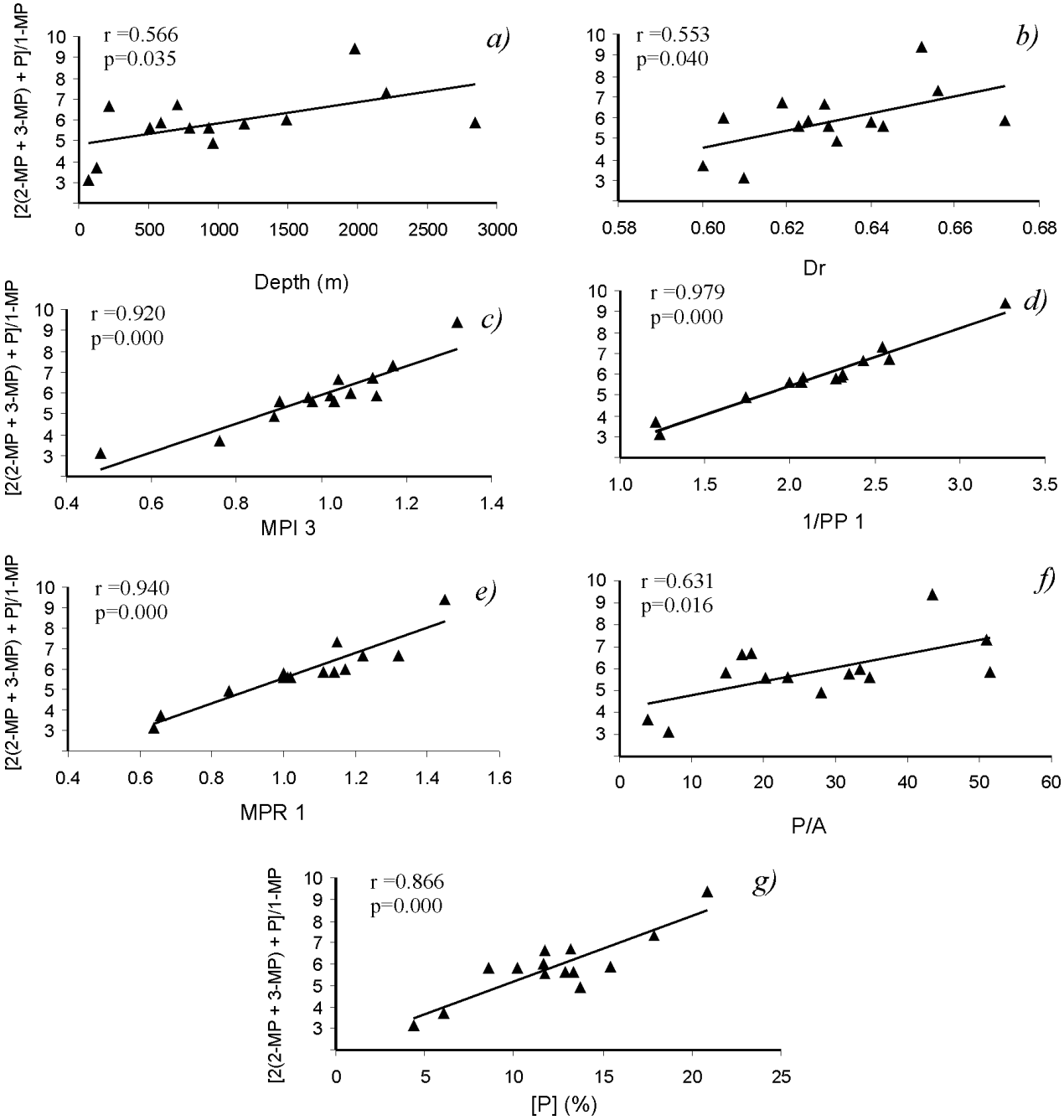

Fig. 3. Correlation diagrams: (*a*) [2(2-MP + 3-MP) + P]/1-MP – depth; and (*b-g*) [2(2-MP + 3-MP) + P]/1-MP – biodegradation independent maturation parameters.

Table 5

The ranges of newly proposed parameters determined for the mentioned three groups of crude oils

Group	Maturation degree (MPI 3 values); ([P])	MPI 3 + 1/PAI 1	[2(2-MP+3-MP)+P]/1-MP
I	High maturity (> 1.00); (> 14.00)	> 1.50	> 5.80
II	Moderate maturity (0.80-1.00); (7.00-14.00)	1.25-1.50	4.00-5.80
III	Low maturity (< 0.80); (< 7.00)	< 1.25	< 4.00

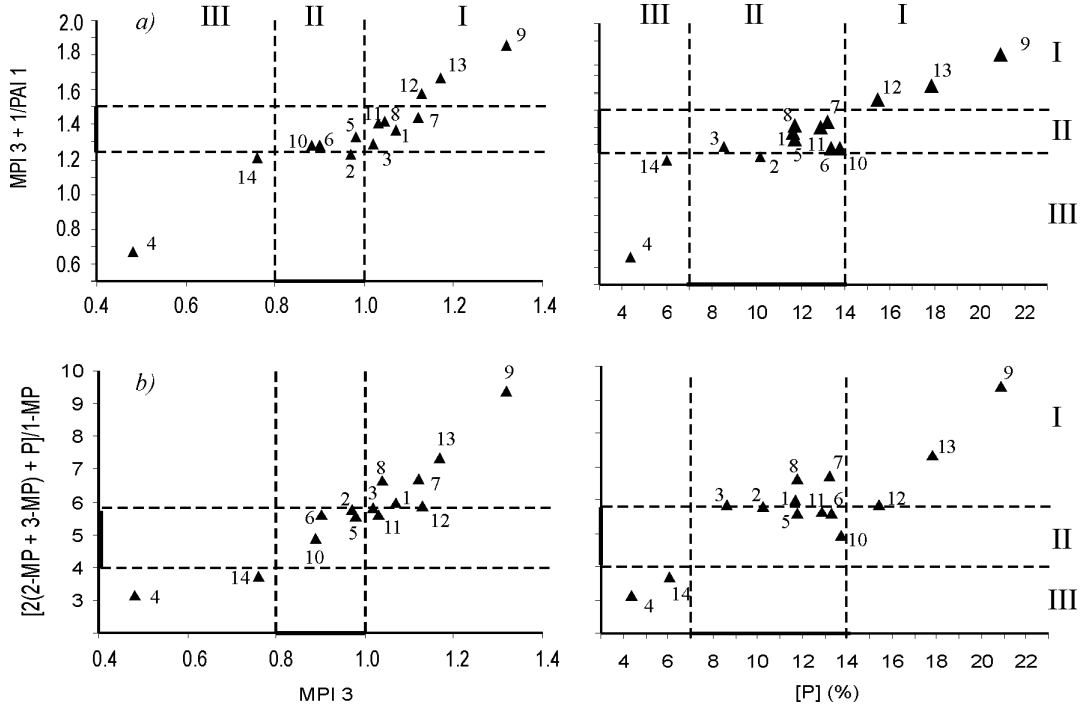

Fig. 4. Classification of the investigated crude oils according to maturity (groups I-III), based on the proportion of phenanthrene in tricyclic aromatic fraction [P], on parameter MPI 3, as well as on two newly proposed maturation parameters: (*a*) MPI 3 + 1/PAI 1, and (*b*) [2(2-MP + 3-MP) + P]/1-MP.

parameters are suggested: for high maturity crude oils (group I) > 1.50 and > 5.80, for moderate maturity crude oils (group II) 1.25-1.50 and 4.00-5.80, and for low maturity crude oils (group III) < 1.25 and < 4.00, respectively.

The observed proportionality of the reservoir rock depths, at which logarithmic [P] - depth curve and the parabolic MP - depth curves reached theoretical maximal values, with the thermodynamic stability of individual isomers, *i.e.*, P (*ca.* 2500 m) > 2-MP (*ca.* 2000 m) > 3-MP ≈ 1-MP (*ca.* 1800 m) > 9-MP (*ca.* 1500 m), suggested that isomerization and dealkylation maturation processes of methylphenanthrene isomers in crude oils of Sakhalin Island oil fields mainly occurred in reservoir rocks themselves. The justifiability of using the proportions of phenanthrene and its methyl isomers in the tricyclic aromatic fraction for the calculation of maturation parameters was thus confirmed.

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